BaNiF$_4$: an electric field-switchable weak antiferromagnet

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We show that in the antiferromagnetic ferroelectric BaNiF$_4$ the Dzyaloshinskii-Moriya interaction leads to a small canting of the magnetic moments, away from the easy axis, resulting in a noncollinear magnetic structure. The canting corresponds to an additional "weak" antiferromagnetic order parameter whose orientation is determined by the polar structural distortion and can be reversed by switching the ferroelectric polarization with an electric field. Our results point the way to a more general coupling mechanism between structural distortions and magnetic order parameters in magnetoelectric multiferroics, which can be exploited in the design of electric field-switchable magnets.

There is great interest in magnetic ferroelectrics, which primarily stems from the possible cross-correlations between their magnetic and dielectric properties [1]. Such *magnetoelectric coupling* facilitates the manipulation of magnetic properties using an electric field and vice versa. Various intriguing effects have been reported so far, ranging from a magnetic field dependence of the dielectric permittivity in various materials including YMnO$_3$ [2], to magnetic phase control using an electric field in HoMnO$_3$ [3], and the reorientation of electric polarization by a magnetic field in TbMnO$_3$ [4].

Of particular appeal, both from the viewpoint of fundamental science and also with respect to possible applications in digital memory technologies, is the switching of *magnetic* domains by an *electric* field and vice versa. Here, the field is used to push the system into a different realization of the same ground state phase. The resulting state continues to be stable even when the field is removed, thus exhibiting the basic requirement for nonvolatile data storage. Such magnetoelectric domain switching has been demonstrated for multiferroic Ni$_3$B$_7$O$_{13}$I, where an electric field can be used to rotate the magnetization by $\pm 90°$ and a magnetic field can switch the polarization into any possible domain configuration [5]. Nevertheless, despite the recent revival of interest in magnetoelectric phenomena, this has, to our knowledge, remained the only report of magnetoelectric domain switching in a single-phase multiferroic. In many multiferroics different mechanisms are driving the magnetic and ferroelectric orders respectively, resulting in only weak coupling between the two order parameters, and disfavoring the possibility of magnetoelectric domain switching. However, electric field-induced magnetization switching has been observed recently in a nano-composite consisting of ferrimagnetic CoFe$_2$O$_4$ pillars embedded in an antiferromagnetic and ferroelectric BiFeO$_3$ matrix [6].

In this letter we introduce a mechanism in which the magnetic order is induced by the ferroelectricity and is therefore intimately coupled to the polarization, allowing controlled switching of the magnetic order parameter by switching the electric polarization using an electric field. We demonstrate this approach using as an example the
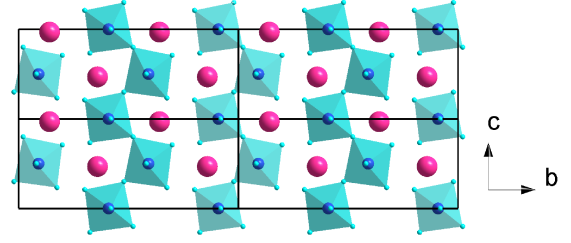

FIG. 1: (Color online) Projection of the BaMF$_4$ structure along the a axis. The M cations are surrounded by fluorine octahedra, which form puckered sheets perpendicular to the b axis, separated by similar sheets of Ba cations. Note that adjacent sheets are shifted relative to each other by half a lattice constant along the a direction.

magnetic ferroelectric BaNiF$_4$, which is representative of a whole class of multiferroic barium fluorides. We show by using both first-principles calculations and symmetry analysis that the polar distortion in this material gives rise to an additional "weak" antiferromagnetic order parameter which is reversed when the ferroelectric polarization is reversed. We suggest the possible experimental observation of this electric field-switchable weak antiferromagnetism and discuss the general implications of our results for magnetoelectric switching phenomena.

BaNiF$_4$ is representative of the isostructural family of barium fluorides with the chemical formula BaMF$_4$, where M can be Mn, Fe, Co, Ni, Zn, or Mg. These compounds were first synthesized in 1968 [7, 8], and crystallize in a base-centered orthorhombic structure with space group $Cmc2_1$ [8] [31], which is shown in Fig. 1. BaMnF$_4$ undergoes an additional structural phase transition at around 250 K (see Ref. 9). Ferroelectric switching has been reported for M=Co, Ni, Zn, and Mg but not for M=Mn and Fe [10]. The systems with M=Mn, Fe, Co and Ni order antiferromagnetically at Néel temperatures around 20-70 K. The magnetic structure derived experimentally for the systems with M=Mn, Fe, Ni is shown in Fig. 2a [11]. The magnetic unit cell is doubled compared to the chemical unit cell, and contains four magnetic M cations, which are arranged in
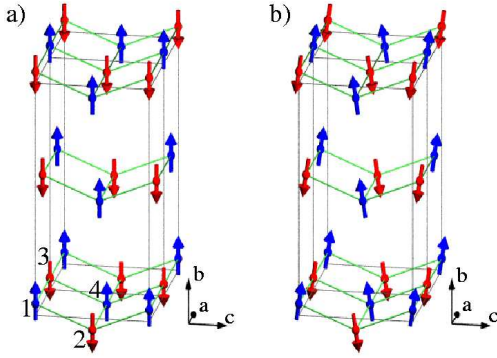
FIG. 2: (Color online) Magnetic structures (not to scale) of BaNiF$_4$ derived from the experimental observations (a) and from our calculation including spin-orbit coupling (b). Gray lines outline the conventional orthorhombic unit cell, green lines show the puckered sheets perpendicular to the b direction, numbers in (a) indicate the 4 magnetic ions in the unit cell.

FIG. 3: (Color online) Dependence of canting angle on the LSDA+U parameters. Black circles correspond to J=0 and red squares to J=1 eV.

sheets perpendicular to the b axis. Within each sheet the cations form a puckered rectangular grid, with the magnetic moments of neighboring cations oriented antiferromagnetically, and all moments aligned parallel to the b axis (c axis for M=Co [12]). The coupling between different sheets is weak, leading to low magnetic ordering temperatures and pronounced two-dimensional behavior [12]. The corresponding magnetic space group is P_a2_1 (P_a2_1' for BaCoF$_4$).

In this letter we focus on the intriguing magnetoelectric and magnetostructural properties of BaNiF$_4$. A detailed comparative study of the structural, electronic, and magnetic properties of the whole series of multiferroic compounds will be reported elsewhere [13]. All calculations presented in this work are performed using the VIENNA AB-INITIO SIMULATION PACKAGE (VASP) [14] employing the projector-augmented wave method [15, 16]. To account for the strong Coulomb interaction between the localized d electrons of the transition metal cations we use the LSDA+U method [17]. For the Hubbard U and intra-atomic exchange parameter J we use typical values of U=4 eV and J=1 eV, and we check the sensitivity of our results with respect to variations of both U and J. We use a plane-wave energy cutoff of 450 eV and a Γ-centered 2×4×2 k-point mesh (divisions with respect to the monoclinic basis vectors of the magnetic unit cell), which is sufficient to obtain converged results for all quantities under consideration.

First we perform a full structural optimization of BaNiF$_4$ within the experimentally observed $Cmc2_1$ symmetry; the structural parameters we obtain agree well with available experimental data [13]. To confirm the experimentally reported magnetic structure we then calculate the energy differences for different relative orientations of the four magnetic sublattices corresponding to
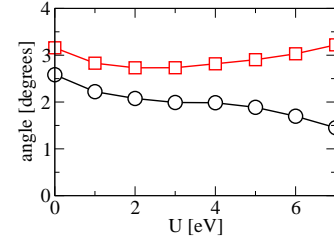
the four magnetic ions in the unit cell and extract the Heisenberg nearest neighbor coupling constants. In these calculations the spin-orbit coupling is neglected. We obtain strong antiferromagnetic nearest neighbor coupling within the buckled planes, J_a=4.4 meV, J_c=3.3 meV [32], consistent with the experimentally observed structure. However, when spin-orbit coupling is included in the calculation, we observe that the collinear spin-configuration shown in Fig. 2a, with all spins aligned along the b direction, is unstable, and that instead the magnetic moments assume a noncollinear configuration where all spins are slightly tilted towards the $\pm c$ direction as shown in Fig. 2b. The tilting angle is about 3 °.

Figure 3 shows the U and J dependence of the canting angle between the magnetic moments of the Ni cations and the b direction. In order to obtain local magnetic moments we integrate the spin-density within spheres of radius 1.2 Å centered at the Ni sites. Our test calculations show that for this radius the integrated spin-density adopts a saturated value of about 1.7 μ_B. It can be seen that within the physically reasonable range of U=2-6 eV there is only a moderate U dependence of the canting angle, whereas it is slightly suppressed by decreasing J. This J dependence is a consequence of the spin-non-diagonal elements introduced into the effective potential by the LSDA+U energy in its most general form [18], which is rotationally invariant with respect to both orbital and spin quantum numbers. It follows from Fig. 3 that within the physically reasonable parameter range of U=2-6 eV and J=0-1 eV the canting angle is 2-3 °.

The small tilting of the magnetic ions can be explained by the antisymmetric exchange or Dzyaloshinskii-Moriya (DM) interaction [19], $E_{ij}^{\mathrm{DM}} = d_{ij} \cdot (s_i \times s_j)$, where s_i is the spin of ion i and d_{ij} is the coupling vector corresponding to the antisymmetric exchange interaction between ions i and j. This interaction occurs only for certain low symmetries and can give rise to "weak ferromagnetism" in otherwise antiferromagnetic materials, where a canting of the two (or more) sublattice magnetizations away from the ideal collinear antiferromagnetic orientation gives rise to a small net magnetization [19, 20]. In the case of BaNiF$_4$ the magnetic space group does not allow the occurrence of weak ferromagnetism but nevertheless there

is a nonzero DM interaction d_c between magnetic nearest neighbors along the c direction [33], whereas the DM interaction between neighboring cations along the a direction vanishes by symmetry.

The canting due to the DM interaction leads to a "weak" antiferromagnetic order parameter $L_c = s_1 + s_2 - s_3 - s_4$, in addition to the experimentally observed (primary) antiferromagnetic order parameter $L_{ab} = s_1 - s_2 - s_3 + s_4$. On a macroscopic level the DM interaction leads to a coupling between L_{ab} and L_c of the form:

$$E_{\text{macro}}^{\text{DM}} = D \cdot (L_{ab} \times L_c) \quad , \qquad (1)$$

where $D = d_c/2$. If we neglect the magnetic single-ion anisotropy contribution to the total energy, the canting angle is given by $\alpha \approx D/4J_c$, from which we obtain a value for D of about $0.7\,\text{meV}$.

Note that a term of the form (1) can also be caused by different orientations of the easy axes for the magnetic moments on different sites. This mechanism is also allowed within the crystallographic and magnetic symmetry of $BaNiF_4$, in addition to the DM interaction described above. Since the following analysis of the magnetoelectric domain switching is independent of the actual microscopic mechanism leading to the term (1), we do not separate these two effects further.

In order to analyze the possibility of magnetoelectric domain switching in $BaNiF_4$ we need to know the symmetry of the corresponding "prototype" phase [20, 21]. Although the paraelectric states of the $BaMF_4$ systems are not accessible experimentally, since all crystals melt before undergoing a ferroelectric phase transition, a nonpolar reference structure has been suggested and used to discuss the ferroelectric switching properties of these systems [22]. This structure has the nonpolar space group $Cmcm$ and can be obtained from the ground state $Cmc2_1$ structure by enforcing a mirror symmetry perpendicular to the c axis. Within this symmetry no canting of the magnetic moments is allowed and the resulting magnetic order corresponds to the collinear spin arrangement shown in Fig. 2a with the magnetic space group P_a2_1/m'. The absence of canting in the centrosymmetric reference structure indicates an intimate connection between the structural distortion and the weak antiferromagnetic order parameter L_c.

In $BaNiF_4$ only two different structural domains are possible, corresponding to the two opposite orientations of the ferroelectric polarization along $\pm c$. Indeed, if we invert the polar mode in our calculation, we observe that for fixed orientation of L_{ab} the orientation of the weak antiferromagnetic order parameter is determined by the orientation of the polarization P (see Fig. 4). This means that a reversal of P by an electric field is accompanied by a reversal of L_c, if during the polarization switching the primary antiferromagnetic order parameter L_{ab} is preserved. Energetically, a reversal of L_c is much more favorable than reversal of L_{ab}, since the latter requires the
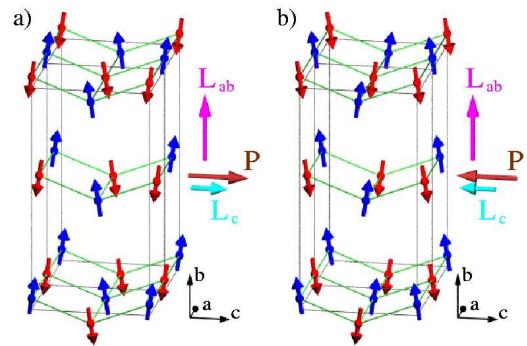

FIG. 4: (Color online) Magnetoelectric switching in $BaNiF_4$. The weak antiferromagnetic order parameter L_c is coupled to the polarization P. Reversal of the polarization from (a) to (b) leads to a reversal of the canting of the magnetic moments and thus to a reversal of L_c.

magnetic moments to rotate by $\sim 180\,^\circ$ through the hard magnetic axis, whereas the reversal of L_c requires only a slight reorientation of the magnetic moments through the easy axis. We therefore propose that the ferroelectric switching in $BaNiF_4$ will be accompanied by a reversal of the weak antiferromagnetic order parameter.

A canted antiferromagnetic structure caused by the antisymmetric exchange interaction has also been proposed in the seminal paper by Moriya [19] for $CuCl_2 \cdot 2H_2O$, and has subsequently been confirmed by several experimental methods including neutron scattering [23], antiferromagnetic resonance measurements [24], and NMR [25]. This shows that a "hidden" order parameter such as L_c can be detected experimentally. However, in order to observe the predicted reversal of L_c by an electric field, an experimental technique is required that allows the distinction between different antiferromagnetic $180\,^\circ$ domains. One such technique, which in addition allows imaging of the antiferromagnetic domain topology, is second-harmonic generation (SHG) [26], which, in fact, has already successfully detected weak antiferromagnetism in $YMnO_3$ [27]. We therefore hope that our work will stimulate experimental efforts to measure the predicted magnetoelectric domain switching in $BaNiF_4$ and related materials.

Magnetic order that is induced by ferroelectricity via the magnetoelectric effect has been suggested for the related system $BaMnF_4$, based on macroscopic symmetry considerations [28]. In $BaMnF_4$ an additional structural phase transition lowers the symmetry so as to allow the linear magnetoelectric effect, which is symmetry-forbidden in $BaNiF_4$. Nevertheless, the microscopic mechanism governing magnetoelectric behavior could be the same in both systems (although a rigorous microscopic study is required to show this unambiguously). The weak antiferromagnetism in $BaNiF_4$ would then be classified as "anti-magnetoelectric effect" [1], mediated by the DM interaction. A related scenario has also been

reported recently for multiferroic $BiFeO_3$, where the DM interaction leads to weak ferromagnetism [20]. Although the linear magnetoelectric effect is symmetry-allowed in this system [34], first principles calculations show that the weak ferromagnetic moment in $BiFeO_3$ is in fact not induced by the ferroelectricity, but is coupled to a non-polar structural mode [20], which exemplifies that symmetry considerations alone cannot provide full insight into the exact coupling mechanism of magnetoelectric systems.

Since the DM interaction can only be nonzero if the midpoint between two magnetic ions is not an inversion center, the occurrence of "weak" magnetic order due to spin-canting should be a rather common phenomenon in magnetic ferroelectrics. The resulting order parameter can in general be ferro- or antiferromagnetic and can be reversed by reversing the structural mode that is responsible for the nonzero DM interaction. If this mode is polar, it can be reversed by an electric field, thus leading to an electric field-switchable magnetic order parameter. Our results for $BaNiF_4$ and our earlier study of $BiFeO_3$ show that the amplitude of the corresponding order parameters are typically of the order of $0.1\,\mu_B$ per magnetic ion, which is about $10\,\%$ of a typical "strong" magnetic order parameter ($\sim 1\,\mu_B$ per magnetic ion), which is easy to measure with modern experimental techniques.

Finally, we compare this with a somewhat converse effect, which is currently attracting a lot of attention, namely the appearance of a small electric polarization in materials where the magnetic order breaks the inversion symmetry of the system. The resulting polarization is then intimately coupled to the magnetic properties [4, 29]. Although the underlying microscopic mechanism is not yet understood, the important role that symmetry plays for this effect is similar to the case of the weak magnetic order discussed in this letter. The magnitude of the resulting electric polarization is around $0.01\,\mu C/cm^2$ [4, 29], which is two to three orders of magnitudes smaller than the spontaneous polarization in typical "strong" ferroelectrics ($\sim$1-10 $\mu C/cm^2$). From this it becomes clear that the "weak" magnetic order that is caused by structural distortions is in comparison a rather large effect and therefore provides a very promising route for achieving practical magnetoelectric coupling effects. In addition, since the weak magnetic order parameter and the ferroelectric polarization are coupled *by symmetry*, it is not necessary that the primary magnetic and ferroelectric order temperatures are close together. The weak magnetic order appears at the Néel temperature but is in fact caused by the structural distortions, which can "freeze in" at much higher temperatures.

In summary, we have shown that the multiferroic system $BaNiF_4$ exhibits an additional "weak" antiferromagnetic order parameter that is coupled to the polar distortion, and can be reversed by reversing the ferroelectric polarization using an electric field. We propose this mechanism as a promising route for achieving magnetoelectric switching behavior in ferroelectric magnets.

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[31] We use the notation of Ref. [30] for crystallographic and magnetic space groups.

[32] We use the form $E_{ij} = -2J_{ij}s_i \cdot s_j$ for the exchange interaction; $J_a = J_{13}$, $J_c = J_{12}$, referring to the indices in Fig. 2a.

[33] We take d_c to be the DM vector $d_{12} = -d_{21}$, referring to the indices shown in Fig. 2a.

[34] If the long-wavelength spin rotation is suppressed, see Ref 20.